

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Intermetallic Compounds and their preparation

We, INTERNATIONAL BUSINESS MACHINES CORPORATION, a Corporation organized and existing under the laws of the State of New York in the United States of America, of Armonk, New York 10504, United States of America (assignees of FREDERICK HOLTZBERG and SIEGFRIED IMENUEL METHFESSEL) do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to rare earth intermetallic compounds and to their preparation.

The rare earth metals and their compounds generally exhibit higher magnetic moments than the iron group metals (e.g. Fe, Co, and Ni) and their compounds, and therefore form an important group of magnetic materials.

The Curie temperatures for the rare earth elements, however, are relatively low, e.g. Dy,  $T_c = 80^\circ\text{K}$  and Gd,  $T_c = 290^\circ\text{K}$ . As a consequence, the application of these elements as magnetic materials has been limited to a low temperature, as in cryogenic systems.

According to the present invention there is provided a rare earth intermetallic compound having the formula  $A_nM$ , where A is Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), or Holmium (Ho) and M is Palladium (Pd) or Platinum (Pt).

A method according to the invention of preparing the rare earth intermetallic compound comprises mixing divided Gadolinium, Terbium, Dysprosium or Holmium with divided Palladium or Platinum and heating the mixture in a sealed crucible which is evacuated or contains an inert atmosphere to a temperature at which the constituents of the

mixture react, and subsequently cooling the mixture to room temperature.

A further method according to the invention of preparing a rare earth intermetallic compound comprises mixing divided Gadolinium, Terbium, Dysprosium or Holmium with divided Palladium or Platinum, supporting the mixture on a cold copper hearth in an inert atmosphere, melting a portion of the mixture which is out of contact with the hearth so causing the constituents of that portion to react, allowing the mixture to solidify and inverting the solidified mixture, repeating the melting, solidifying and inverting a plurality of times, and allowing the melt to cool to room temperature.

The invention will now be described by way of example. The following rare earth intermetallic compounds are examples of the invention:

Gd <sub>5</sub> Pd <sub>3</sub>	(71.4 at. (78.7 wt.) per cent Gd)	60
Tb <sub>5</sub> Pd <sub>3</sub>	(71.4 at. (78.9 wt.) per cent Tb)	
Dy <sub>5</sub> Pd <sub>3</sub>	(71.4 at. (79.2 wt.) per cent Dy)	
Ho <sub>5</sub> Pd <sub>3</sub>	(71.4 at. (79.6 wt.) per cent Ho)	
Gd <sub>5</sub> Pt <sub>3</sub>	(71.4 at. (66.8 wt.) per cent Gd)	
Tb <sub>5</sub> Pt <sub>3</sub>	(71.4 at. (67.2 wt.) per cent Tb)	65
Dy <sub>5</sub> Pt <sub>3</sub>	(71.4 at. (67.6 wt.) per cent Dy)	
Ho <sub>5</sub> Pt <sub>3</sub>	(71.4 at. (67.9 wt.) per cent Ho)	

These rare earth intermetallic compounds are prepared by mixing 5 moles of the rare earth element Gd, Tb, Dy, or Ho with 2 moles of either Pd or Pt in finely divided form and then heating the mixture to melt and react the component elements. The heating is accomplished by using either of the following methods.

The first method involves placing the mixture in an inert refractory metal crucible, made of tantalum or molybdenum for example,

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which is evacuated and sealed (e.g., by cold welding). The crucible is now placed in a quartz vacuum apparatus surrounded by a radio-frequency induction heating coil. An atmosphere of helium or argon may be used inside the crucible in place of the vacuum. Energy is delivered to the coil at a rate such that the crucible is raised to a temperature of between 1400°C and 1600°C. This temperature is maintained until the reaction is completed. The supply of energy is stopped and the crucible rapidly cools to room temperature. There is a finite solubility of tantalum in the melt, and the second method (which is an arc melting process) of preparing these compounds is preferred.

In the second method appropriate quantities of the rare earth and transition metal are mixed in finely divided form in amounts corresponding to those desired in the final compound, are pressed into a pellet for convenient handling. This pellet is then placed in an arc furnace the chamber of which is evacuated and flushed with an inert gas, such as argon, neon, krypton, xenon, or helium, three times to purge the chamber. The furnace has a movable cathode which is used to strike an arc to a water-cooled copper hearth (anode) which contains several wells or shallow depressions to hold the mixture being melted and reacted. The arc is struck to the anode in the vicinity of the reactants, which are fused by the heat of the arc. The cathode is mounted through a ball and swivel joint and the molten material can be stirred by precessing the cathode tip around the periphery of the melt.

After the mixture has been fused, the arc is interrupted and the melt once solidified is turned over in the well and remelted in the arc. By repeatedly turning and melting the resulting compound can be made homogeneous. A temperature in excess of 3500°C can readily be generated and such a temperature is more than sufficient to fuse the metals Gd, Tb, Ho, and Pd. However, a thin solid layer of the materials being fused is kept on the cold anode surface ensuring that the melt itself does not contact the metal of the anode. Alloying of the anode and the melt is thus avoided.

The resulting rare earth intermetallic compounds are brittle metallic materials which form a protective oxide coating when exposed to the atmosphere.

The compounds have the following magnetic properties;  $Gd_2Pd_3$  is ferromagnetic below 61°C with a saturation moment of 197 emu per gram in agreement with the moment calculated for an atomic moment of 7 Bohr magnetons per Gd atom. The saturation magnetization decreases with increasing temperature,  $T$ , according to the  $(T)^{3/2}$  law up to  $T=0.8 T_c$ . The Curie temperature,  $T_c$ , where the magnetic moment disappears is

334°K.  $Gd_2Pd_3$  is a soft magnetic material with a coercive force of less than 100 oersteds and the magnetization  $O_{H,T}$  saturates at constant temperature  $T$  with a field  $H$  to the saturation value  $O_{\infty,T}$  following the law

$$O_{H,T} = O_{\infty,T} \left(1 - \frac{a}{H}\right)^n \quad \text{with a magnetic hardness}$$

$$a = \frac{(O_{\infty,T} - O_{H,T})^n}{O_{\infty,T}} = 110 \text{ oersteds, which}$$

value is lower than a  $Gd=359$  oe. for pure gadolinium metal.

Since the  $Gd_2Pd_3$  has a coercive force and hardness lower than Gd metal and a saturation magnetization higher than most iron group metals and their alloys (approximately 25,000 gauss at 0°K compared with the approximate value for iron of 21,000 gauss)  $Gd_2Pd_3$  is useful in electronic and magnetic devices such as transformers or relays. At room temperature (20°C)  $Gd_2Pd_3$  has a magnetic moment of 45% of the saturation value available. (Gd is paramagnetic at this temperature.) Since the Curie temperature is 61°C, and the variation of the magnetization with temperature is high in the region of room temperature,  $Gd_2Pd_3$  is useful as a core material in thermal switching, control, and safety devices.

In contrast to  $Gd_2Pd_3$ , the compounds  $Tb_2Pd_3$ ,  $Dy_2Pd_3$ , and  $Ho_2Pd_3$  have paramagnetic-metamagnetic transitions (Neel points  $T_N$ ) below liquid nitrogen temperature (e.g., the  $T_N$  for  $Dy_2Pd_3$  is 41°K;  $Tb_2Pd_3$  is 62°K and  $Ho_2Pd_3$  is 33°K), and become ferromagnetic at still lower Curie temperatures (e.g.,  $Dy_2Pd_3$ ,  $T_c=25^\circ K$ ;  $Tb_2Pd_3$ ,  $T_c=30^\circ K$ ; and  $Ho_2Pd_3$ ,  $T_c=10^\circ K$ ) with a high coercive force (e.g., the  $H_c$  for  $Tb_2Pd_3$  is 12,800 o.e.;  $Dy_2Pd_3$  is 9700 oe. and  $Ho_2Pd_3$  is 1300 oe.). The extreme magnetic hardness makes these compounds useful as permanent magnets in cryogenic circuits and devices operating around liquid helium temperature (4.2°K) which is the normal operating temperature for cryogenic circuitry.

The similarity in chemical properties between Pd and Pt is reflected in the similarity between the magnetic properties of  $A_2Pd_3$  and  $A_2Pt_3$ , for example,  $Gd_2Pd_3$  and  $Gd_2Pt_3$  are isostructural and have the same ferromagnetic Curie temperature.

Rare earth intermetallic compounds having the formula  $A_2M_3$  where A is Gd, Tb, Dy or Ho and M is Pd or Pt have been prepared in accordance with the following Examples and found to be ferromagnetic.

#### EXAMPLE I

$Gd_2Pd_3$  (71.4 at. (78.7 wt.) per cent-Gd)  
7.87 grams of Gd metal filings and 2.13 grams of Pd powder were thoroughly mixed and pressed into pellets which were placed

5 in a tantalum crucible which was evacuated and sealed by cold welding. The crucible was placed on a pedestal in an evacuated quartz cylinder and heated to 1600°C for 2 minutes with a radio frequency induction heating coil and rapidly cooled to room temperature. The resulting product was Gd<sub>2</sub>Pd<sub>3</sub>.

#### EXAMPLE II

10 Gd<sub>2</sub>Pd<sub>3</sub> (71.4 at. (78.7 wt.) per cent Gd)  
7.87 grams of Gd metal filings and 2.13 grams of Pd powder were mixed and pressed into a pellet. The pellet was placed in a well of a water-cooled copper hearth of an arc melting furnace. The furnace chamber was evacuated and flushed with argon gas three times to purge the chamber of reactive gases. An arc was struck between the tungsten cathode and the water-cooled hearth of the arc furnace. A current of 150 amps at 40 volts liquefied the mixture in about 10 seconds. The melt was stirred by precessing the cathode around the periphery of the melt for about 30 seconds, and then the power was turned off and the melt allowed to solidify and cool. The sample was then inverted and the above arc melting, cooling and turning procedure was repeated three times until a homogeneous product was obtained and allowed to cool rapidly to room temperature. Since the sample was in direct contact with the cold copper hearth, the cooling was essentially a quench from the molten state. Micro-metallurgical examination revealed the completeness of the reaction by showing a single phase compound. This compound was Gd<sub>2</sub>Pd<sub>3</sub>.

#### EXAMPLE III

40 Tb<sub>2</sub>Pd<sub>3</sub> (71.4 at. (78.9 wt.) per cent Tb)  
The process of Example II was repeated except that 7.89 grams of Tb and 2.11 grams of Pd were used instead of the Gd and Pd of Example II. The resulting compound was Tb<sub>2</sub>Pd<sub>3</sub>.

#### EXAMPLE IV

45 Dy<sub>2</sub>Pd<sub>3</sub> (71.4 at. (79.2 wt.) per cent Dy)  
The process of Example II was repeated except that 7.92 grams of Dy and 2.08 grams of Pd were substituted for the Gd and Pd of Example II. The resulting compound was Dy<sub>2</sub>Pd<sub>3</sub>.

#### EXAMPLE V

55 Ho<sub>2</sub>Pd<sub>3</sub> (71.4 at. (79.6 wt.) per cent Ho)  
The procedure of Example II was repeated except that 7.96 grams of Ho and 2.04 grams of Pd were substituted for the Gd and Pd used in Example II. The resulting product was Ho<sub>2</sub>Pd<sub>3</sub>.

#### EXAMPLE VI

60 Gd<sub>2</sub>Pt<sub>3</sub> (71.4 at. (66.8 wt.) per cent Gd)  
6.68 grams of Gd metal filings and 3.32

grams of platinum powder were mixed and pressed into a pellet. This pellet was placed in the well of a water-cooled copper hearth of an arc melting furnace. The furnace chamber was evacuated and flushed with argon gas three times to purge the chamber of reactive gases. An arc was struck between the tungsten cathode and the water-cooled hearth of the arc furnace. A current of 150 amperes at 40 volts liquified the sample in about 10 minutes. The melt was stirred by precessing the cathode around the periphery of the melt for about 30 seconds, and then the power was turned off and the melted sample allowed to cool and solidify. The sample was then inverted and the above arc-melting, cooling, and turning procedure repeated three times until a homogeneous product was obtained and cooled rapidly to room temperature. Since the sample was in direct contact with the cold copper hearth, the cooling was essentially a quench from the molten state. Micro-metallurgical examination revealed the completeness of the reaction by showing a single phase compound. This compound was Gd<sub>2</sub>Pt<sub>3</sub>.

#### EXAMPLE VII

Tb<sub>2</sub>Pt<sub>3</sub> (71.4 at. (67.2 wt.) per cent Tb)  
The process of Example VI was repeated except that 6.72 grams of Tb and 3.28 grams of Pt were used instead of the Gd and Pt of Example VI. The resulting compound was Tb<sub>2</sub>Pt<sub>3</sub>.

#### EXAMPLE VIII

Dy<sub>2</sub>Pt<sub>3</sub> (71.4 at. (67.6 wt.) per cent Dy)  
The process of Example VI was repeated except that 6.75 grams of Dy and 3.24 grams of Pt were substituted for the Gd and Pt of Example VI. The resulting compound was Dy<sub>2</sub>Pt<sub>3</sub>.

#### EXAMPLE IX

Ho<sub>2</sub>Pt<sub>3</sub> (71.4 at. (67.9 wt.) per cent Ho)  
The procedure of Example VI was repeated except that 6.79 grams of Ho and 3.21 grams of Pt were substituted for the Gd and Pt used in Example VI. The resulting product was Ho<sub>2</sub>Pt<sub>3</sub>.

#### WHAT WE CLAIM IS:—

1. A rare earth intermetallic compound having the formula A<sub>2</sub>M<sub>3</sub> wherein A is the rare earth Gd, Tb, Dy, or Ho, and M is the transition metal Pd or Pt. 110
2. The rare earth intermetallic compound Gd<sub>2</sub>Pd<sub>3</sub> (71.4 at. (78.7 wt.) per cent Gd).
3. The rare earth intermetallic compound Tb<sub>2</sub>Pd<sub>3</sub> (71.4 at. (78.9 wt.) per cent Tb). 115
4. The rare earth intermetallic compound Dy<sub>2</sub>Pd<sub>3</sub> (71.4 at. (79.2 wt.) per cent Dy).
5. The rare earth intermetallic compound Ho<sub>2</sub>Pd<sub>3</sub> (71.4 at. (79.6 wt.) per cent Ho). 120
6. The rare earth intermetallic compound

- Gd<sub>3</sub>Pt<sub>2</sub> (71.4 at. (66.8 wt.) per cent Gd).  
 7. The rare earth intermetallic compound Tb<sub>3</sub>Pt<sub>2</sub> (71.4 at. (67.2 wt.) per cent Tb).  
 8. The rare earth intermetallic compound Dy<sub>3</sub>Pt<sub>2</sub> (71.4 at. (67.6 wt.) per cent Dy).  
 9. The rare earth intermetallic compound Ho<sub>3</sub>Pt<sub>2</sub> (71.4 at. (67.9 wt.) per cent Ho).  
 10. A process of preparing the rare earth intermetallic compound according to any one of the preceding claims, comprising mixing divided Gadolinium, Terbium, Dysprosium or Holmium with divided Palladium or Platinum and heating the mixture, in a sealed crucible which is evacuated or contains an inert atmosphere to a temperature at which the constituents of the mixture react, and subsequently cooling the mixture to room temperature.  
 11. A process according to claim 10, wherein the constituents of the mixture are mixed in a molar ratio of 5:2 and the crucible is made of tantalum and sealed by cold welding.  
 12. A process of preparing rare earth intermetallic compound according to any one of claims 1 to 9 comprising mixing divided Gadolinium, Terbium Dysprosium or Holmium with divided Palladium or Platinum, supporting the mixture on a cold copper hearth in an inert atmosphere, melting a portion of the mixture which is out of contact with the hearth so causing the constituents of that portion to react, allowing the mixture to solidify and inverting the solidified mixture, repeating the melting, solidifying and inverting a plurality of times, and allowing the melt to cool to room temperature.  
 13. A process according to claim 12, wherein the constituents of the mixture are mixed in a molar ratio of 5:2, wherein the inert atmosphere consists of argon and wherein the melting, solidifying and inverting are repeated three times.  
 14. A process of preparing a rare earth intermetallic compound substantially as hereinbefore described with reference to any one of the Examples.

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